THE STOCHASTIC ROTATION OPERATOR AND NUCLEAR MAGNETIC RELAXATION PROCESSES

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The application of the stochastic rotation operator technique to the calculation of orientational correlation functions is extended so as to allow the calculation of the relaxation times that occur in nuclear magnetic resonance theory. Explicit expressions are given for times arising from spin-rotational interactions when the relaxing molecule is spherical, linear or a symmetric rotator.

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A study of the rotational Brownian motion of an asymmetric top with inclusion of inertial effects was based on the stochastic rotation operator $R(t)$ which specifies at time t the orientation of a body-fixed coordinate frame with respect to a laboratory frame.[1] The rotation operator satisfies the equation

$$\frac{dR(t)}{dt} = -i\left(\vec{J}\cdot\vec{\omega}(t)\right)R(t), \tag{1}$$

where $\vec{\omega}(t)$ is the angular velocity of the body referred to the body frame. The solution of (1) consists of a slowly varying ensemble average $\langle R(t)\rangle$ about which there are random fluctuations, and the solution is expressed as

$$R(t) = \left(I + \varepsilon F^{(1)}(t) + \varepsilon^2 F^{(2)}(t) + \cdots\right)\langle R(t)\rangle, \tag{2}$$

where I is the identity operator and ε is a small dimensionless parameter. The non-stochastic $\langle R(t)\rangle$ obeys an equation

$$\frac{d\langle R(t)\rangle}{dt} = \left(\varepsilon\Omega^{(1)}(t) + \varepsilon^2\Omega^{(2)}(t) + \varepsilon^3\Omega^{(3)}(t) + \cdots\right)\langle R(t)\rangle. \tag{3}$$

The Euler-Langevin equations satisfied by the components of $\vec{\omega}(t)$ provide the value of $\langle\omega_i(t_1)\,\omega_j(t_2)\rangle$ and we may then deduce from (1), (2) and (3) expressions for $\varepsilon F^{(1)}(t)$, $\varepsilon^2 F^{(2)}(t)$, ..., $\varepsilon\Omega^{(1)}(t)$, $\varepsilon^2\Omega^{(2)}(t)$, ... for substitution into (2) and (3).

In applications of this theory to complex polarizability arising from orientational polarization of dielectrics[2] we were concerned only with the after-effect operator which is defined as the solution of (3) with

the initial condition $\langle R(0)\rangle = I$. The after-effect function may be employed to calculate correlation functions. Thus the correlation function for spherical harmonics

$$\left\langle Y^{*}_{jm}(\beta(0),\alpha(0))\, Y_{jm'}(\beta(t),\alpha(t))\right\rangle = \frac{1}{4\pi}\left(\langle R(t)\rangle^{j}_{m'm}\right)^{*} \qquad (4)$$

$1/(4\pi)$ - times the complex conjugate of the $m'm$-element of $\langle R(t)\rangle$ in the representation with basis elements Y_{js}. To treat the case of dielectric polarization one puts $j=1$, $m=m'=0$. However, (4) has wider applications; for example, $j=2$ is applicable to Raman scattering.

In the context of nuclear magnetic relaxation eq. (4) may be employed in the calculation of

a. spin lattice relaxation time[3]

b. contribution of intramolecular dipole-dipole interactions to the nuclear magnetic relaxation rate of identical nuclei[4]

c. contribution of quadrupole interactions to the nuclear magnetic relaxation rate of identical nuclei.[4]

Equation (4) cannot be applied to the contribution of spin-rotational interactions to the nuclear magnetic relaxation rate. The difficulty here is that we are no longer concerned with $\langle R(t)\rangle$ but with the ensemble average of a function of both the orientational and the angular velocity variables.

Let us therefore consider the contribution of spin-rotational interactions to nuclear magnetic relaxation of identical nuclei in identical molecules. If $\vec{I}$ is the spin operator of a nucleus and $\hbar\vec{J}$ the angular momentum of the molecule that contains the nucleus, the spin-rotational Hamiltonian of the nucleus is expressible as $\vec{I}\cdot\vec{C}\cdot\vec{J}$.

We denote by $b_{-1\nu}, b_{0\nu}, b_{1\nu}$ the spherical components of $C_{\mu\nu}$. The body frame is taken through the centre of mass and in the directions of the principal axes of inertia, the corresponding moments being I_1, I_2, I_3. The contributions from the spin-rotational interactions to the reciprocals of the longitudinal and transverse relaxation times are equal in the extreme narrowing case and their common value T_{sr}^{-1} is given by[5]

$$\frac{1}{T_{sr}} = 2c(0), \qquad (5)$$

where

$$c(s) = (3\hbar^2)^{-1}\sum_{\mu,\nu=1}^{3}\sum_{m,n=-1}^{1}(-)^{m} b_{m\mu}\, b_{n\nu}\, I_\mu I_\nu \left(\int_0^\infty e^{-st}\langle R(t)\omega_\mu(t)\omega_\nu(0)\rangle dt\right)_{n,-m}. \qquad (6)$$

The spin-rotational correlation time is likewise given by

$$\tau_{sr} = \frac{3\hbar^2}{kT}\,\frac{c(0)}{\sum_{\mu=1}^{3}\sum_{m=-1}^{1}(-)^{m} b_{-m\mu}\, b_{m\mu}\, I_\mu}. \qquad (7)$$

In eq. (6) we have denoted by $n,-m$ the $n,-m$-element with respect to the basis $Y_{1,-1}(\beta(0),\alpha(0))$, $Y_{10}(\beta(0),\alpha(0))$, $Y_{11}(\beta(0),\alpha(0))$, where $\alpha(0)$, $\beta(0)$ are the Euler angles that give the direction at time zero of the third molecular axis with respect to the laboratory frame. Since $R(t)$ depends not only on the orientation but also, through (1), on $\vec{\omega}(t)$, we see that we need for the evaluation of $c(s)$ the ensemble average of a function of orientational and angular velocity variables that cannot be expressed as the product of a function of orientational variables and a function of angular velocity variables.

From eq. (2)

$$\langle R(t)\omega_\mu(t)\omega_\nu(0)\rangle = \left(\langle\omega_\mu(t)\omega_\nu(0)\rangle + \langle\varepsilon F^{(1)}(t)\omega_\mu(t)\omega_\nu(0)\rangle + \langle\varepsilon^2 F^{(2)}(t)\omega_\mu(t)\omega_\nu(0)\rangle + \cdots\right)\langle R(t)\rangle. \tag{8}$$

The terms $\varepsilon^{2n+1} F^{(2n+1)}(t)\omega_\mu(t)\omega_\nu(0)$ contain an odd number of ω_i's. Now when the molecule is spherical or linear, ω_i is centred and Gaussian and $\langle \varepsilon^{2n+1} F^{(2n+1)}(t)\omega_\mu(t)\omega_\nu(0)\rangle$ consequently vanishes. When the molecule is spherical, the value of $\langle R(t)\rangle$ is known[2,3] and the values of the $\varepsilon^{2n} F^{(2n)}(t)$ may be found, as explained earlier. An expression for $\langle R(t)\omega_\mu(t)\omega_\nu(0)\rangle$ has then been deduced up to terms proportional to ε^4 from (8). In the Laplace transform of $\langle R(t)\omega_\mu(t)\omega_\nu(0)\rangle$ difficulties arise for $s=0$ in the terms proportional to $J_\mu J_\nu$. Fortunately these yield no contribution to the summations in (6). For our purposes all that we require is the relation

$$\lim_{s\to 0}\int_0^\infty e^{-st}\langle R(t)\omega_\mu(t)\omega_\nu(0)\rangle_{j=1}\,dt = \frac{kT}{I\mathcal{B}}\left\{\delta_{\mu\nu} I + \gamma\left[-\delta_{\mu\nu} I - \frac{i}{2}(\vec{J}\cdot\vec{e}_\mu\times\vec{e}_\nu) + \gamma^2\left[\frac{13}{6}\delta_{\mu\nu} I + \frac{13}{12} i(\vec{J}\cdot\vec{e}_\mu\times\vec{e}_\nu)\right]\right.\right. \tag{9}$$
$$\left.\left. - \frac{1}{2} J_\mu J_\nu + \frac{1}{4} J_\mu J_\nu + \frac{1}{6}\gamma^2 J_\mu J_\nu + \cdots\right\},$$

where $\mathcal{B}$ is a frictional constant such that the couple resisting the motion is $I\mathcal{B}$ times the angular velocity and $\gamma = kT/(I\mathcal{B}^2)$, a small dimensionless constant, I denoting here the moment of inertia.

To find T_{st} from (5) and (6) we suppose that all the nuclei are in equivalent positions in the molecule and we take the third body frame axis through the nucleus in which we are interested. This allows us to write

$$b_{\pm 1,1} = \mp\frac{C_\perp}{\sqrt{2}}, \quad b_{\pm 1,2} = \frac{iC_\perp}{\sqrt{2}}, \quad b_{03} = C_{11}$$

$$b_{01} = b_{02} = b_{\pm 1,3} = 0.$$

From these equations and (9) we obtain

$$\frac{1}{T_{st}} = \frac{2IkT}{3\hbar^2\mathcal{B}}\left\{\left(C_{11}^2 + 2C_\perp^2\right) - \gamma\left(C_\perp - C_{11}\right)^2 + \frac{13}{6}\gamma^2\left(C_\perp - C_{11}\right)^2 + \cdots\right\}. \tag{10}$$

Similarly we deduce from (7) that, if we write $\xi = C_\perp/C_{11}$,

$$\tau_{st} = \frac{1}{\mathcal{B}}\left\{1 - \gamma\frac{(\xi-1)^2}{2\xi^2+1} + \frac{13}{6}\gamma^2\frac{(\xi-1)^2}{2\xi^2+1} + \cdots\right\}. \tag{11}$$

Equations (10) and (11) agree with the results of Hubbard.[6]

The investigation of the problem for the linear rotator by this method is quite lengthy. The calculations have been performed to relative order γ^2 but the final result

$$\frac{1}{T_{st}} = \frac{4kTIC_\perp^2}{3\hbar^2\mathcal{B}}$$

is independent of γ. The corresponding spin-rotational correlation time is $\mathcal{B}^{-1}$.

For the symmetric top model of the molecule the above method yields

$$\frac{1}{T_{st}} = \frac{2kT}{3\hbar^2}\left\{\frac{2I_1 C_\perp^2}{\mathcal{B}_1 + \mathcal{D}_1 + \mathcal{D}_3} + \frac{I_3 C_{11}^2}{\mathcal{B}_3 + 2\mathcal{D}_1}\right.$$
$$+ kT\left[\left(\frac{2}{\mathcal{B}_1^3} + \frac{2I_1}{I_3\mathcal{B}_1^2\mathcal{B}_3} - \frac{2I_3}{I_1\mathcal{B}_1^2(\mathcal{B}_1+\mathcal{B}_3)}\right)C_\perp^2\right. \tag{12}$$
$$\left.\left. + \frac{2I_3\left(C_{11}^2 + 2C_\perp C_{11}\right)}{I_1\mathcal{B}_1\mathcal{B}_3(\mathcal{B}_1+\mathcal{B}_3)}\right]\right\} + \cdots$$

for a nucleus lying on the axis of symmetry, which is taken to be the third coordinate axis, so that $I_2 = I_1$. The frictional constants are B_1, B_1, B_3, and

$$D_1 = \frac{kT}{I_1 B_1} \quad , \quad D_3 = \frac{kT}{I_3 B_3} .$$

The spin-rotational correlation time τ_{sr} is obtained from (12) on replacing the multiplying factor $2kT/(3\hbar^2)$ by $(I_1 C_\perp^2 + I_3 C_\parallel^2)^{-1}$.

For the asymmetric model of the rotating molecule an expression for the Laplace transform of $\langle R(t) c_2(\xi) c_2(0) \rangle$ has been derived up to terms of relative order γ. The difficulty of the $J_\mu J_\nu$ terms is now more serious as we can no longer say that they will give no contribution to $G(\omega)$. In order to complete the study of this problem it will be necessary to calculate $\langle R(t) \rangle$ for the asymmetric molecule to a higher degree of accuracy. In principle the method of doing this is available.[1]

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